



Al/Pb lightweight grids prepared by molten salt electroless plating for application in lead-acid batteries



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HIGHLIGHTS

- We presented a new cheaper molten salt system for electroless plating Pb on Al.
- The metal bath process can amend the pores of Pb coating after electroless plating.
- The metal bath process can regulate the composition and thickness of Pb coating.
- Al/Pb grids have excellent performances and can be well used in lead-acid battery.

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ABSTRACT

In this paper, a lightweight Pb plated Al (Al/Pb) grid was prepared by molten salt electroless plating. The SEM and bonding strength test show that the lead coating is deposited with a smooth surface and firm combination. CV test shows that the electrochemical properties of Al/Pb electrodes are stable. 2.0 V single-cell flooded lead-acid batteries with Al/Pb grids as negative collectors are assembled and the performances including 20 h capacity, rate capacity, cycle life, internal resistance are investigated. The results show that the cycle life of Al/Pb-grid cells is about 475 cycles and can meet the requirement of lead-acid batteries. Al/Pb grids are conducive to the refinement of PbSO₄ grain, and thereby reduce the internal resistance of battery and advance the utilization of active mass. Moreover, weight of Al/Pb grid is only 55.4% of the conventional-grid. In this way, mass specific capacity of Al/Pb-grid negatives is 17.8% higher and the utilization of active mass is 6.5% higher than conventional-grid negatives.

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1. Introduction

Lead-acid battery is one of the most successful electrochemical systems that ever developed, and no other battery is yet able to replace it in the field of energy storage, albeit batteries based on other chemistries are rapidly catching up [1]. As is known to all, the specific energy of lead-acid battery is very low, generally about 30 Wh kg⁻¹, which is only about 1/2 of Ni-metal hydride batteries and 1/4 of lithium-ion batteries. Besides the high density of Pb active materials, it is mainly because of its large use of inert matter [2] (lead alloy grid materials). Therefore, it is very important for us to conduct the research so as to replace the heavy and costly lead alloy grids with lightweight one.

The research of lightweight grids for lead-acid battery was mainly devoted to electrodeposition an lead film on the substrates with low specific gravity and good electric conductivity, such as copper [3,4], aluminum [5,6], titanium [7], carbon [8] and some other light materials [9–12]. Relatively speaking, Ti and Cu are expensive, which will increase the cost of lead-acid battery. For this reason, Pb plating Cu grids are only used in special battery at present, such as tank and submarine battery. Compared with metal base grids, the mechanical strength of carbon grid is very poor which hindered its application. Aluminum, due to the advantages of lightweight, high strength, excellent conductivity and low price, is considered to be one of the best choices [13]. But the deposition of continuous lead coatings on aluminum from aqueous solutions is very difficult because of the insulating and dense oxide film, which is very easy to form on the aluminum surface. What's more, Pb and Al are very difficult to form a solid solution.

Generally, Pb (or Pb alloy) plating on the surface of Al (or Al alloy) in aqueous solution needs pretreatment [14]. Firstly, plating

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one or two transition layers on the surface of Al matrix, which often contains zinc, copper and nickel [15,16], then lead electro-plating. The process is long and complex, and the quality of Al/Pb composite material prepared with this method is difficult to control. Most serious problem is that there are always lots of pores and defects on the coating [15], and the metallic elements of transition layer may enter into the electrolyte, deteriorating the performance of lead-acid batteries. L.A. Yolshina [17,18] and Timmons [19] electrolessly deposited a lead layer on the surface of aluminum in chloride molten salt (components: LiCl, KCl and PbCl₂) without any transition layer. This method avoided the adverse effects of aluminum oxide and easily realized the direct deposition of lead on Al matrix with a series of simple processes. But the lead film was not smooth and there were many pores on the surface. This may lead to serious corrosion of aluminum matrix because of the galvanic effect if the pores were penetrated by electrolyte. In addition, the using of LiCl, which is deliquescent and expensive, may make the plating process difficult and increase the cost of batteries.

Our work was committed to improving this technology through developing a new molten salt system (components PbCl₂ + CaCl₂ + NaCl + SnCl₂) of the electroless plating process followed by metal bath, and a compact and composition adjustable Pb-alloy film can be directly obtained on Al substrate [20]. In this study, a series of Al/Pb grids were prepared and characterized. Then, the performance of 2.0 V single-cell flooded lead-acid batteries, with Al/Pb grids as the negative current collectors, were investigated.

2. Experimental

2.1. Preparation of lead-plating aluminum grids (Al/Pb grids)

Preparation of Al/Pb grids with the method of molten salt electroless plating has three steps – pretreatment, molten-salt plating, metal bath.

Pretreatment: the pure aluminum matrix were chemical polished by the alkaline slurry (components: NaOH 400 g L⁻¹, NaNO₃ 300 g L⁻¹, Na₃PO₄ 20 g L⁻¹, Processing temperature: 100 °C, Processing time: 20 s) which was widely used in industry. Then, the matrix were immersed in the so called four sodium solution [21] (components: NaOH 20 g L⁻¹, Na₂CO₃ 20 g L⁻¹, Na₃PO₄ 10 g L⁻¹, and Na₂SiO₃ 4 g L⁻¹) for 10 min to remove the oil, drying at 80 °C after washed by deionized water.

Molten-salt Plating: the pure aluminum substrates after pretreatment were immersed in the mixed molten-salt for 90 s, then, the raw product of Al/Pb grid was prepared. All the chlorine salts used were inexpensive and commonly available. And in this experiment, all the chlorine salts, bought from commercial company, are AR grade.

Metal Bath: the raw Al/Pb grid was immersed in the particular molten Pb alloy (components: Pb99.58 wt.%, Ca0.10 wt.%, Sn0.20 wt.%, Al0.02 wt.%, Ag0.10 wt.%, 400 °C) for 10 s to improve the coating properties and wash away the chlorides, then the Al/Pb lightweight grid was obtained (Fig. 1).

2.2. Preparation of 2.0 V flooded lead-acid batteries

For battery testing, 2.0 V single-cell flooded units were assembled using one negative plate with Al/Pb grids as the negative collectors sandwiched between two regular positive plates (Al/Pb-grid cell, shows in Fig. 1). The collector has a size of 4.0 cm × 6.8 cm (height × width) and geometric area of 27.2 cm². The thickness was 0.30 cm for the positive plate and 0.20 cm for the negative plate. The Pb alloy strap (about 5 mm × 2 mm) was welded on Al/Pb plate

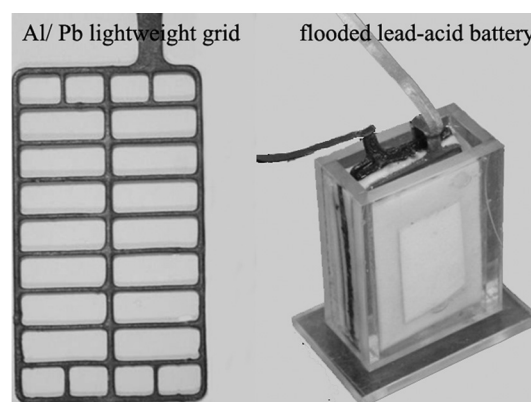


Fig. 1. The Al/Pb lightweight grid and 2.0 V single-cell flooded lead-acid battery.

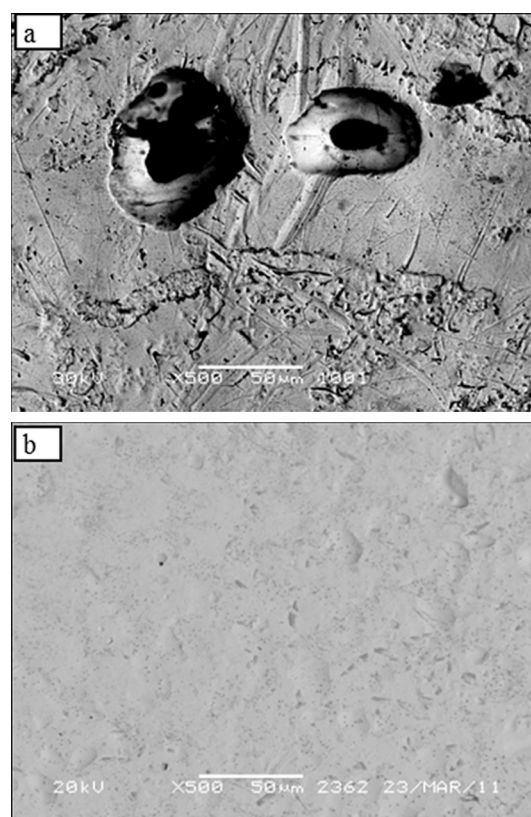


Fig. 2. Surface morphology of Al/Pb electrode before and after metal bath. a–Before metal bath; b–after metal bath.

terminal with a lead solder carefully. The reference samples were the cells with conventional Pb-alloy grid (components: Pb 99.68 wt.%, Ca0.1 wt.%, Sn0.20 wt.%, Al0.02 wt.%) (conventional-grid cell) produced by Henan Yuguang Gold & Lead Co., Ltd. China.

2.3. Instruments analysis

The electrochemical experiments were carried out with a three-electrode system. The counter electrode was a Pt plate with a geometric area of 16.00 cm². Electrochemical experiments such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a PARSTAT 2273 electrochemical workstation controlled by the powersuit software. The frequency interval of EIS measurement was from 10⁵ to 10⁻² Hz,

and the AC amplitude is 5 mV. Battery testing was performed using LAND battery test system. JSM-6360F Scanning Electron Microscope (SEM) was used to observe the microscopic surface morphology of as-prepared Al/Pb electrode.

3. Results and discussion

3.1. Coating properties analysis

3.1.1. The coating composition and morphology of Al/Pb electrode

In the molten salt electroless plating process, Pb^{2+} , in the form of PbCl_2 in the molten salt, was reduced to metal Pb by Al on the surface of electrode, and the product Pb deposited on the fresh surface, replacing the element Al. The chemical composition of the coating obtained was pure Pb, which was confirmed by the former work [20].

The surface morphology (shows in Fig. 2a) of initial Al/Pb electrode obtained after the molten salt electroless plating showed that, there were many pores on the surface of lead coating, which was also reported by L.A. Yolshina [17]. The lead coating was detached from Al base 10 h after being immersed in the 5 M H_2SO_4 solution, as the pores would be the corrosion channels and seriously affect the corrosion resistance of the Al/Pb electrode.

In this work, a metal bath process was added. The process of metal bath could make the lead coating to recrystallize in metal melt and remove the defects formed in the process of molten salt electroless plating [22]. As shown in Fig. 2b, all the pores and defects vanished and a smooth, flat, dense lead coating was obtained after metal bath. What's more, the composition and thickness of the coating on Al substrate can be conveniently adjusted by changing the composition of the melt used in metal bath process and the process parameters, which were propitious to meet a variety of purposes.

3.1.2. The bonding strength of lead coating

Grids in lead-acid batteries, supporting the active substances, need to bear the deformation of active materials in the charge and discharge processes. Therefore, the lead coating must have good bonding strength with the Al matrix, otherwise it would fall off during the operation.

The metallograph was used to observe the cross section morphology of the lead coating. A clear transition layer (with thickness of 5–10 μm) was found in the interface (as shown in Fig. 3). The EDS test results showed that the composition of this transition layer was Al–Pb–Sn ternary alloy (Al 69.02 wt.%, Pb

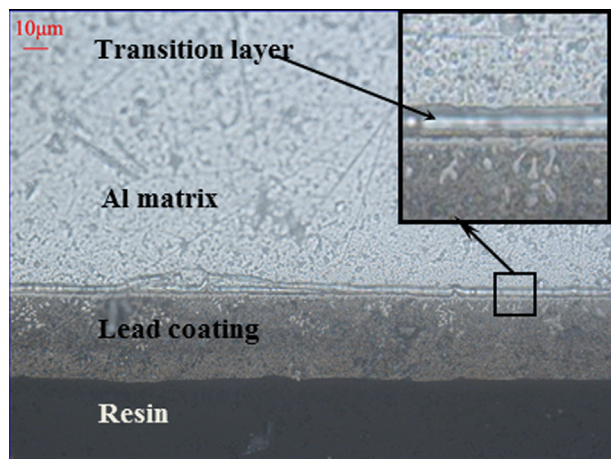


Fig. 3. The metallographic photos of the cross section of Al/Pb electrode.

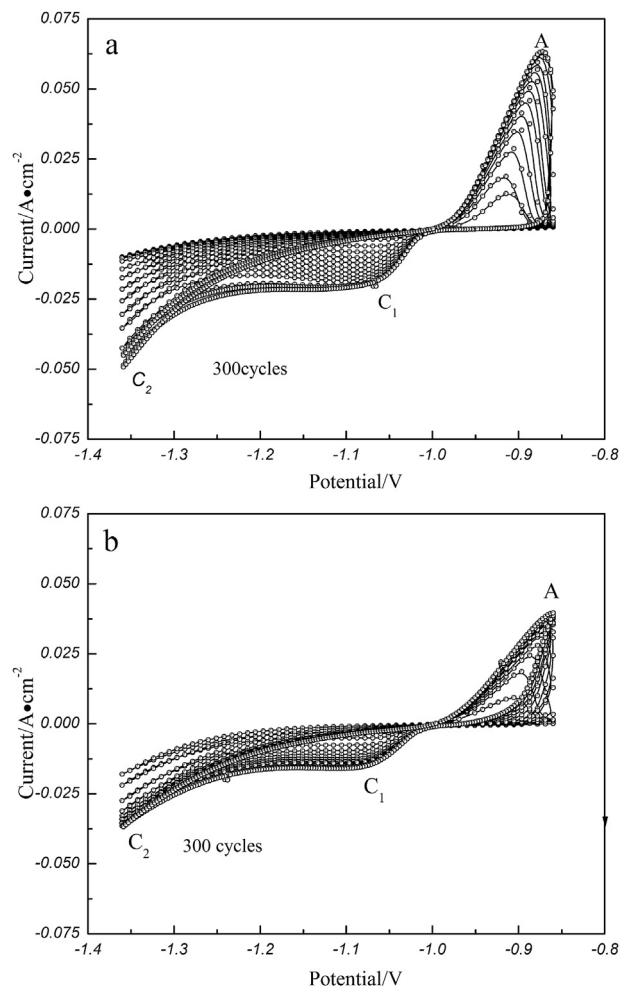


Fig. 4. Voltammograms between –1.36 and –0.86 (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) for Al/Pb electrode and Pb alloy electrode in 5 M H_2SO_4 solution at 25 °C. a – Pb alloy electrode, b – Al/Pb electrode.

11.87 wt.%, Sn 19.11 wt.%). This means the Al matrix and the lead coating were contacted with a metallurgical combination. Tested average bonding strength was no less than 2.6 MPa, which was better than most electroplated coatings.

3.1.3. Cycle life of Al/Pb electrode

Cyclic voltammetry was used here to evaluate the cycle life of lead coating on the surface of Al/Pb electrode. Fig. 4 shows a series of curves of the 300-cycle cyclic voltammetry between –1.36 V and –0.86 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) at 25 °C in 5 M H_2SO_4 solution, the scanning rate was fixed at 20 mV s^{-1} . In general, the electrode showed obvious reaction characteristics of lead or lead alloy. In the positive scanning, Pb was oxidized to PbSO_4 at –0.96 V to –0.86 V (peak A) [23]; In the negative scanning, the formed PbSO_4 was reduced to sponge Pb at –0.95 V to –1.11 V (peak C_1), and hydrogen was released since –1.11 V. It was observed that there weren't any other reactions occurred in the 300 cycles process, and the change of peak currents was neglectable after 150 cycles. The peak current of Al/Pb electrode (peak A and C_1) was much smaller than regular Pb alloy electrode which indicated that Al/Pb electrode had a more stable electrochemical performance. This was mainly because of the existence of Ag who could improve the corrosion resistance of the Pb electrode. In addition, the Al/Pb electrode was immersed in 5 M H_2SO_4 solution and the lead–alloy coating was kept intact after

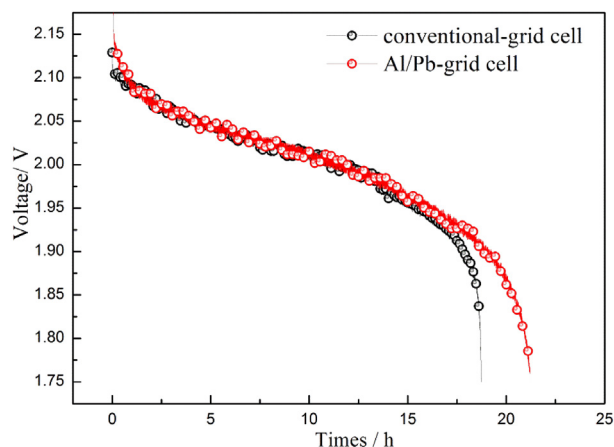


Fig. 5. The discharge–voltage behavior under 20 h rate capacity test.

more than one year. These features depicted that the electrochemical properties of lead coating were very stable when used as the negative grid in lead-acid battery.

3.2. Performance test of 2.0 V flooded lead-acid batteries

Through the above discussions, an Al/Pb composite negative grid with smooth surface, firm combination, stable electrochemical properties which meet the requirements of lead-acid batteries was obtained. Therefore, the negative-limit-capacity flooded lead-acid single cells which used Al/Pb grid as the negative current collector were produced and the performances including 20 h rate capacity, rate capability, cycle life, internal resistance were investigated. In these tests, the design capacity of the Al/Pb-grid cells and conventional-grid cells were all 2.42 Ah for 20 h rate.

3.2.1. The 20 h rate capacity test (C_{20})

The profile of the 20 h rate capacity test consist of following processes: (i) Full charged at constant current of $3I_{20}$ A to 2.4 V followed by a constant voltage of 2.4 V for 10 h (I_{20} was gotten by calculation according to design capacity); (ii) Left standing open-circuited for 5 h (iii) Discharging at constant current of I_{20} A to the cut-off voltage of 1.75 V.

The initial capacity test results showed in Fig. 5. It was found that the 20 h rate capacities of the Al/Pb-grid cell and conventional-grid cell were 2627.2 mAh and 2341.2 mAh, respectively. Then, we can calculate the mass specific capacity and the utilization of negative active materials (NAM, as shown in Table 1). The negative mass specific capacity of Al/Pb-grid cell was 121.5 mAh g^{-1} , which was 17.8% higher than conventional-grid cell. And the improvement of the mass specific capacity of Al/Pb-grid cell can be attributed to the following two aspects: For one thing, the weight of Al/Pb grid was 4.12 g, which was just 55.4% of Pb-alloy grid; For another, the utilization of NAM was 61.1% for Al/Pb-grid cell, which was 6.5% higher than conventional one. The different composition (especially Sn and Ag) and crystal structure of the coating surface would make a certain contribution. During formation and cycling, tin

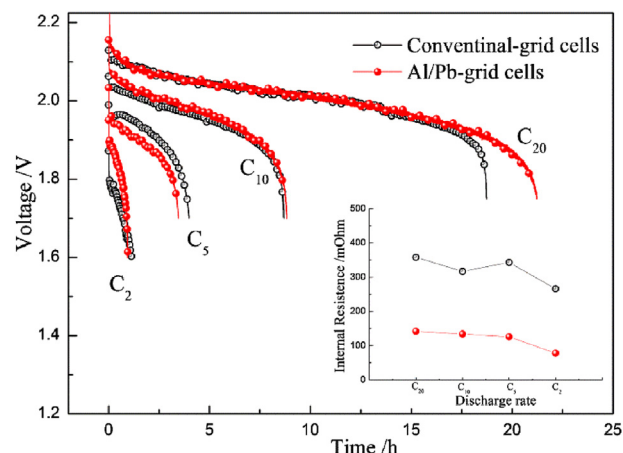


Fig. 6. The rate discharge behavior of Al/Pb-grid cells and conventional-grid cells.

would dissolve in bath solution and brought a beneficial effect on the capacity [24,25], but tin also existed in conventional-grid with the same content. For this consideration, we guess silver is the main reason for increasing capacity. The silver, regardless of the concentration, would be transferred to the negative active material, which may enable the NAMs to conduct current even in a deeply discharged state, improving battery recharge [25,26].

3.2.2. Rated capacity

The rate capacity test was conducted based on the GB/T 19639.1-2005 to evaluate the performance of the batteries under different discharge hour rates. The profile consists of two periods: (i) Full charge: a constant current charge at $3I_{20}$ A to 2.4 V, followed by a constant voltage charge at 2.4 V for 10 h (ii) Rate discharge: a constant current discharge corresponding to the discharge hour rate (including C_{20} , C_{10} , C_5 , C_2) until the cell voltage was lowered to the specified voltage (the specified cut-off voltage were 1.75 V, 1.70 V, 1.65 V and 1.60 V for C_{20} , C_{10} , C_5 , C_2 , respectively). Then, we could build the Peukert plot for the conventional-grid and Al/Pb-grid cells based on these data.

The performance characteristics of the cells at different discharge rates (including C_{20} , C_{10} , C_5 , C_2) are shown in Fig. 6. It was found that the discharge time of Al/Pb-grid cells was longer than conventional-grid cells at low discharge rate (C_{20}), but a little shorter at high discharge rate (C_5 , C_2). The Al/Pb-grid cells had specific energy close to 40.5 Wh kg^{-1} at the C_{20} rate, however, conventional cells was only 31.2 Wh kg^{-1} . The initial voltage drop was observed during discharge process which suggested that the Al/Pb-grid cells had lower internal resistances compared with conventional-grid cells neither at low discharging rate nor high discharging rate (as shown in the insert map). The Peukert constant of Al/Pb-grid cell was 1.34, which was higher than the conventional-grid cell (as showed in Fig. 7.). The result indicated that the high rate discharge capability (HRDC) of Al/Pb-grid cells was poorer. This was rather different with previous researches which reported that the good grid conductivity would improve the HRDC. We suspected that the welding point would be rosin joint

Table 1
Capacity of 2.0 V flooded lead-acid batteries (C_{20}).

	Negative plate (g)	Negative grid (g)	Negative active materials (g)	20 h rate capacity (mAh)	Utilization of active mass (%)	Negative mass specific capacity (mAh g^{-1})
Conventional-grid cell	24.94	7.44	17.50	2341.2	54.6	103.1
Al/Pb-grid cell	21.62	4.12	17.50	2627.2	61.1	121.5

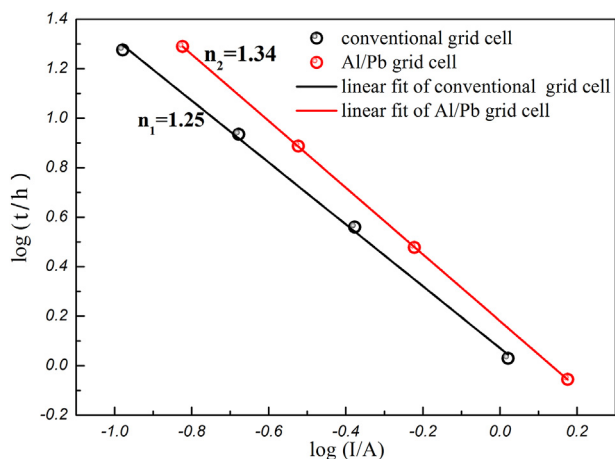


Fig. 7. The peukert plot for conventional- and Al/Pb-grid cells.

because Pb was difficult to weld onto the thin Pb coating on Al substrate. The poor conductivity of the welding point dragged the cell's high rate discharge capability.

3.2.3. Cycle life

According to the GB/T 19639.1-2005 5.18.2 standard, the cycle life test profile comprises: (i) Full charge as described above. (ii) Constant current discharge at $5I_{20}$ A for 2 h, followed by a constant current charge at $2I_{20}$ A for 6 h. These discharge and charge processes consist of one cycle. (iii) A constant current discharge at $5I_{20}$ A to the cut-off voltage of 1.70 V when comes to 25th, 50th, 75th...cycles, and this discharge capacity was recorded. End loop if the measured capacity was lower than $0.5C_{20}$. Fig. 8 was the variation curves of discharge capacities of Al/Pb-grid cell in cycle life test. The capacities declined gradually at the beginning and then maintained stable. Finally, cycle life of Al/Pb-grid cell was about 475 cycles that meet the requirements of the GB/T 19639.1-2005 standard.

3.2.4. Battery internal resistance

Fig. 9 shows the internal resistance comparison between the conventional-grid cell and Al/Pb-grid cell in cycle life test. It showed that the resistance value of Al/Pb-grid cell was about

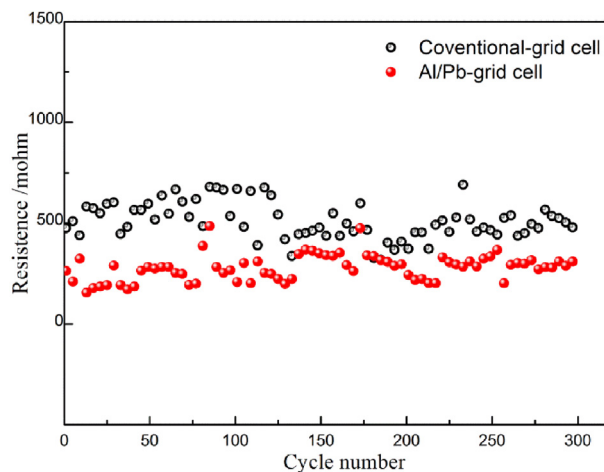


Fig. 9. The internal resistances in 300 cycles life test.

300 mΩ, which was much smaller than that of conventional-grid cell.

The impedance parameters of partial state-of-charge (SoC = 50%) conventional- and Al/Pb-grid negative plates were measured potentiostatically under -1.36 V over a wide range of frequencies (10^{-1} Hz to 10^4 Hz) in 5 M H_2SO_4 solution. Fig. 10 shows the Nyquist diagram and the insert diagram was the adopted equivalent-circuit [27,28] for simulation. In which, R_e is the sum of electrode resistance and solution resistance; R_1 denotes the resistance of electrochemical reaction; C is the absorption capacitance; R_2 is the ions transferring resistance through the $PbSO_4$ layer. An obvious inductance, L , is observed at high frequency, which can be ascribed to the charge relaxation on electroactive materials containing heterogeneity or energy disorder [29]. Q is the constant phase element, and its impedance can be written as:

$$Z = \frac{1}{Q(j\omega)^n}$$

where, $j = (-1)^{1/2}$ and n represents the deviation from the ideal behavior, $n = 1$ for the perfect capacitors and $n = 0$ for the pure resistors.

In the $PbSO_4$ reduction process, the $PbSO_4$ crystals dissolve and ionize to Pb^{2+} and SO_4^{2-} ions, followed by the diffusion of the SO_4^{2-}

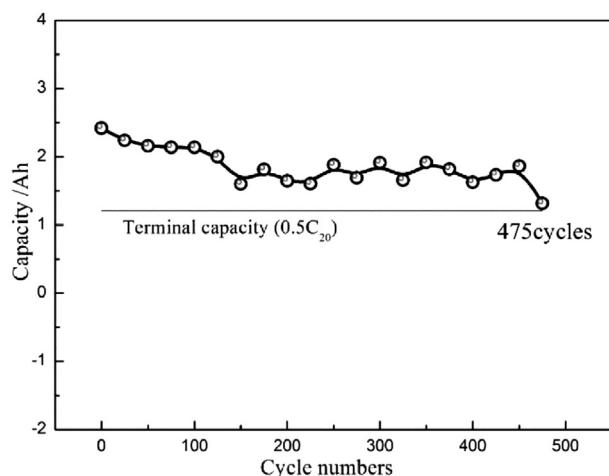


Fig. 8. The discharge capacities variation of Al/Pb-grid cell under cycle life test.

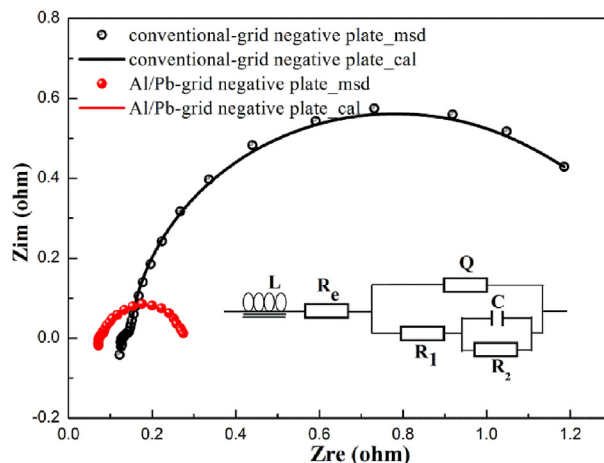


Fig. 10. Nyquist plots of Al/Pb-grid and conventional-grid negative plates with 27.2 cm^2 surface area in 5 M H_2SO_4 at -0.9 V.

Table 2Fit parameters for conventional and Al/Pb-grid negative plates in 5 M H₂SO₄ under −0.9 V conditions.

	<i>L</i> (Henri)	<i>R</i> _e (Ω)	<i>Q</i> (S sec ⁿ)	<i>n</i>	<i>R</i> ₁ (Ω)	<i>C</i> (F)	<i>R</i> ₂ (Ω)	χ ²
Pb-grid negative	5.48E-7	0.1268	0.1879	0.8047	0.0380	0.0224	1.26	6.08E-4
Al/Pb-grid negative	3.04E-7	0.0719	0.3115	0.7949	0.0308	0.1871	0.1753	3.84E-4

ions towards bulk solution and the Pb²⁺ ions towards the reaction surface at which the Pb²⁺ ions get electrons to reduce. The fitting results are shown in Table 2. The results showed that the reaction rate of Pb/PbSO₄ depends on the diffusion of SO₄^{2−} ions towards bulk solution and Pb²⁺ ions towards the reaction surface at high potential (−1.36 V). This was consistent with the former research [30]. Comparison the two sets of data showed that the ions transferring resistance (*R*₂) of Al/Pb-grid negative plate was much smaller. The SEM photograph (as shown in Fig. 11) showed that the PbSO₄ particles on the surface of Al/Pb-grid negative plate were a little smaller than that on the conventional one. Yonglang Guo [30] researched the electrochemical behavior of PbSO₄ with different structures and proposed that the large PbSO₄ crystals impeded the diffusion of Pb²⁺ and SO₄^{2−} ions due to the diffusion distance of ions to the reaction surface extent. That is to say, the negative plate with small PbSO₄ crystals would have lower ion transferring resistance. Moreover, the double layer capacitor of Al/Pb-grid negative plate was larger, which means that the Al/Pb-grid negative plate has a looser structure and higher porosity, this may be beneficial to the electrochemical reaction. Subsequently, the looser structure could provide more adsorption site, and then enlarge the adsorption capacitor. Because of good conductivity of Al matrix, *R*_e of Al/Pb-grid negative plate was reduced obviously. For these reasons, the internal resistance of Al/Pb-grid cell was reduced comparing with the conventional one.

4. Conclusion

Al/Pb composite electrode materials were produced by molten salt electroless deposition. This Al/Pb electrode has a smooth surface, firm combination, stable electrochemical properties that can meet the application requirements of high concentrations sulfuric acid system like lead-acid battery.

Performance characteristics of 2.0 V single-cell flooded lead-acid batteries with Al/Pb electrodes as negative collectors were investigated. On one hand, the Al/Pb grid could reduce the electrical resistance of plate, and the existence of Ag may be conducive to the refinement of PbSO₄ grain and improve its conductivity, and then reduce the internal resistance. On the other hand, the weight of Al/Pb grid was only 55.4% of Pb-alloy grid, which can reduce the weight of the cell. With the combined action of the two aspects, the internal resistance of Al/Pb-grid lead-acid battery is significantly reduced compared with conventional-grid batteries, the utilization of NAMs and the mass specific capacity of Al/Pb-grid cell were advanced. In addition, cycle life of the Al/Pb-grid cell was about 475 cycles that could meet the requirement of lead-acid batteries.

The present study suggests that Al/Pb composite material produced by molten salt electroless deposition is suitable for negative grid of lead-acid batteries, if the welding problem of plate terminal is resolved. In addition, it is also expected to be applied in the field

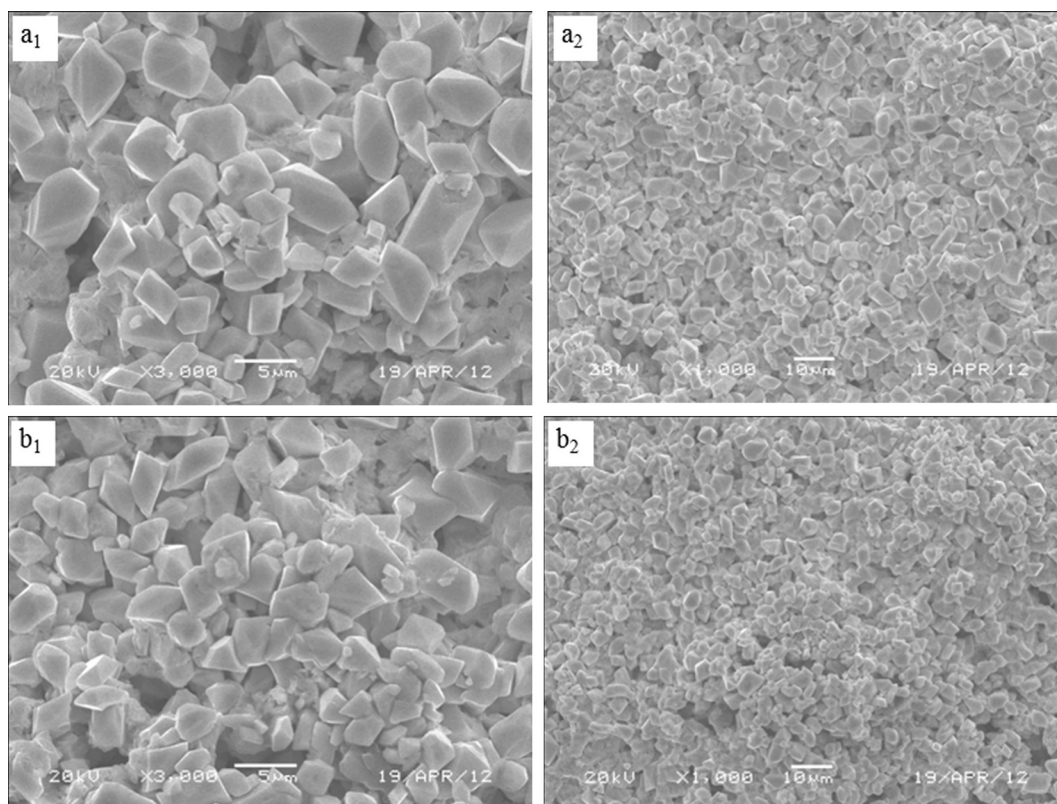


Fig. 11. The PbSO₄ morphology on the surface of negative plates. a1, a2 – conventional-grid negative plate; b1, b2 – Al/Pb-grid negative plate.

of copper, zinc electrowinning and organic electrosynthesis to replace the conventional Pb electrodes.

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